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Organic synthesis applied to space sciences

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Abstract. About 160 molecules have been detected in the interstellar medium, the comae and the atmospheres of planets. The presence of these compounds leads to imagine a chemistry of these media to explain the formation of these species and to predict the possible presence of other ones. Many of them have never been synthesized or isolated in labs and their preparation can be challenging, up to necessitate news reactions or special equipments.

INTRODUCTION

The recording of the Infrared (IR), Ultraviolet (UV) and Microwave (MW) spectra of many places of the Universe shows signals corresponding to complex mixtures of molecules. The identification of about 150 molecules in the interstellar medium (ISM) [1], of dozens in comae and in the planetary atmospheres (Jupiter, Saturn, Neptune, Venus, Titan (the largest moon of Saturn), . . .) has generated many attempts to know how they are formed and eventually decomposed, and to predict which other compounds could be observed in these media.

The understanding of the chemistry of the ISM, of planetary atmospheres including the Earth is probably one of the most intriguing research subjects. For a long time, the region between the stars was considered to be too hostile to contain quantities of molecules, but at the end of the 1960s, ammonia [2], water [3, 4] and formaldehyde [5] were observed. So far, about 150 molecules (Table 1) and 100 isotopomers have been discovered in the ISM, and numerous reviews tried to explain the synthesis of these compounds in this medium [6–10].

The ISM is a very complex medium, not at all homogeneous in all the areas of the space. It is usually extremely tenuous, with densities ranging from a few thousand to a few hundred million particles per cubic meter. The matter consists of about 99% gas and 1% dust (probably silicate and carbonaceous) by mass. As a result of primordial nucleosynthesis, the gas is roughly 92% hydrogen and 8% helium by number of nuclei, with additional heavier elements present in trace amounts. Oxygen, Carbon, Nitrogen, Neon, Magnesium, Silicium, Iron, Sulfur and Argon are the most important atoms. Among the molecules discovered up-to-now, neutral molecules, cations, radicals and more recently anions were observed. Most of them are small by the number of atoms. Chemistry in the ISM can be performed in the gas phase or on the grains since solid mixtures containing H_2O, CO_2, CO, NH_3, CH_3OH or CH_4 were identified via IR spectroscopy toward the dense cloud TMC-1 [11]. Even with only 1% of the interstellar matter, the dust components play a key role in the chemistry of the ISM, and particularly shield molecules in the gas phase from the destructive external UV radiation field. Up to now it has generally been accepted that most of the interstellar molecules have been synthesized in the gaseous phase but this assumption could change in the future.

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When comets approach the Sun, many compounds are produced by solar irradiation. In comets and comae, water, carbon monoxide, hydrogen cyanide, formaldehyde, methanol, ammonia, methane, acetylene, ethane, hydrogen sulfide, CH and CN radicals, acetic acid, methyl formate, carbon dimer, carbon monosulfide, sulfur cation and many other compounds have been detected [12].

Similarly the chemistry of planetary atmospheres is rich and complex. Thirty years ago, the IRIS instruments on the Voyager spacecraft had already shown the presence of many organic compounds in Titan's atmosphere [13, 14]. More recently, complex mixtures of molecules have been discovered in the high atmosphere of Titan: gaseous N_2-CH_4 mixtures are photolyzed at a very high altitude to produce many molecules of different sizes up to oligomeric and polymeric compounds (tholins) [15]. So far, diazote, methane, ethane, hydrogen cyanide, cyanoacetylene, acetonitrile, acetylene, butadiyne, carbon monoxide, carbon dioxide and, more recently, benzene have been detected in the atmosphere of Titan. In the atmospheres of Jupiter or Saturn where hydrogen and helium are the main components, methane, ethane, acetylene, benzene, water, ammonia, phosphine, arsine, germane, hydrogen sulfide and several other minor components are present [16, 17].

To understand the chemistry of these medias, it would be very useful to reproduce the experimental conditions. However, many parameters (the very low temperature of the tenuous clouds of the ISM, the solar irradiation of comets and the photolysis of the gases in comae or in planetary atmospheres) are not easily reproducible in our labs. On the other hand, thermodynamically stable compounds formed in these media can be kinetically very unstable compounds in the condensed phase, even at the relatively low temperature of liquid nitrogen, and the analysis of products and photoproducts can be more than difficult. Many components of these media are commercially available or easy to prepare but several of them are still unknown and cannot be synthesized in standard conditions. On the list of the detected interstellar molecules reported on Table 1, are indicated *in italics* the compounds which have never been (or cannot be) isolated in pure form in the condensed phase. Although several species have been generated in the gaseous phase and directly analyzed, to have in hand the non-radical neutral species is necessary to perform a complete spectroscopic identification and to be able to study their chemistry or photochemistry. For their preparation, special experimental conditions or new chemical reactions are sometimes necessary. We describe here examples of the synthesis in labs of some detected compounds or of possible candidates of these media. Successively, we report the synthesis of 1-alkynenitriles, their chemistry and photochemistry, the synthesis of adducts of cyanoacetylene with water, ammonia or hydrogen sulfide, the studies on the isomers of acetonitrile, the generation and characterization of cations, anions and radicals; the problem of the analysis and detection of polycyclic aromatic hydrocarbons (PAH) or tholins will then be discussed.

1. CYANOACETYLENE AND CYANOPOLYYNES

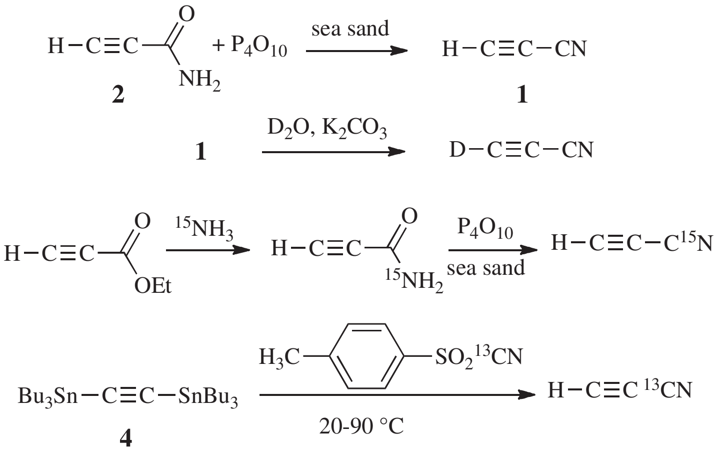
1.1 Synthesis

As indicated in Table 1, cyanoacetylene and five cyanopolyynes have been detected in the ISM [18]. On Titan, cyanoacetylene **1** (HC_3N) is one of the most intriguing compounds because it shows a high enhancement from the equator to the north pole at the time of Voyager measurements [19]. HC_3N, as the first member of the cyanoalkyne's family, has been predicted by photochemical models to be one of the main links between the gas phase and the photochemical haze seen at high altitudes. Origin and evolution of this compound on Titan's atmosphere are key questions and the isotopic composition could give an answer [20, 21]. Thus, to differentiate between primordial escape phenomena and photochemical fractionation, it is interesting to study D/H and $^{15}N/^{14}N$ ratio of more molecules than the two already studied N_2 and HCN. The detection and determination of the mean abundance of such species by spectroscopy are conditioned by the knowledge of band intensities of the expected species which is dependent on the availability to isolate pure isotopic samples. The synthesis of labeled derivatives can allow the identification of photoproducts or to precise the reactions pathways of the photoproducts.

Table 1. List of the detected interstellar molecules (those which have never been isolated in pure form in labs in the condensed phase are in *italic*).

Number of Atoms	Molecule
2	*AlCl*, *AlF*, $\mathrm{C_2}$, CF+, *CH* (and *CH+*), *CN*, CO (and *CO+*), *CP*, CS, FeO, $\mathrm{H_2}$, HCl, HF, *HN*, *HO*, KCl, $\mathrm{N_2}$, NO, NS, NaCl, $\mathrm{O_2}$, PN, *PO*, *SH* (and *SH+*), SO (and *SO+*), *SiC*, *SiN*, *SiO*, *SiS*.
3	$\mathit{H_3^+}$, *AlNC*, $\mathit{CH_2}$, $\mathit{C_3}$, $\mathit{C_2H}$, $\mathit{C_2O}$, $\mathit{C_2S}$, $\mathrm{CO_2}$, $\mathrm{H_2C}$, $\mathrm{H_2O}$, $\mathrm{H_2S}$, HCN, *HCO* (and *HCO+*), HCP, *HCS+*, HNC, $\mathit{HN_2^+}$, *HNO*, $\mathit{HOC^+}$, KCN, MgCN, MgNC, $\mathit{NH_2}$, $\mathit{N_2H^+}$, $\mathrm{N_2O}$, NaCN, OCS, $\mathrm{CO_2}$, $\mathit{c\text{-}SiC_2}$, *SiCN*, *SiNC*, $\mathrm{SO_2}$.
4	$\mathit{CH_3}$, $\mathit{l\text{-}C_3H}$, $\mathit{c\text{-}C_3H}$, $\mathit{C_3N}$, $\mathit{C_3O}$, $\mathit{C_3S}$, $\mathrm{C_2H_2}$, $\mathit{H_3O^+}$, $\mathit{H_2CN}$, $\mathit{HCNH^+}$, $\mathrm{H_2CO}$, $\mathrm{H_2CS}$, *HCCN*, $\mathit{HCNH^+}$, $\mathit{HOCO^+}$, HNCO, HNCS, $\mathrm{NH_3}$, $\mathit{c\text{-}SiC_3}$.
5	$\mathit{C_5}$, $\mathit{C_4N}$, $\mathrm{CH_4}$, $\mathit{c\text{-}C_3H_2}$, $\mathrm{l\text{-}H_2C_3}$, $\mathit{H_2CCN}$, $\mathrm{H_2C_2O}$, $\mathrm{H_2CNH}$, $\mathit{H_2COH+}$, $\mathit{C_4H}$ (and $\mathit{C_4H^-}$), $\mathrm{HC_3N}$, HCCNC, HCOOH, $\mathit{HNC_3}$, $\mathrm{NH_2CN}$, $\mathit{SiC_4}$, $\mathrm{SiH_4}$.
6	$\mathrm{c\text{-}C_3H_2O}$, $\mathrm{C_2H_4}$, $\mathrm{CH_3CN}$, $\mathrm{CH_3NC}$, $\mathrm{CH_3OH}$, $\mathrm{CH_3SH}$, $\mathit{l}\text{-}\mathrm{H_2C_4}$, $\mathit{HC_3NH^+}$, $\mathrm{HCONH_2}$, $\mathit{C_5H}$, $\mathit{C_5O}$, $\mathit{C_5N}$, $\mathrm{HC_2CHO}$, $\mathit{HC_4N}$, $\mathrm{CH_2CNH}$.
7	$\mathrm{c\text{-}C_2H_4O}$, $\mathrm{CH_3C_2H}$, $\mathrm{H_3CNH_2}$, $\mathrm{CH_2CHCN}$, $\mathrm{H_2CHCOH}$, $\mathit{C_6H}$ (and $\mathit{C_6H^-}$), $\mathrm{HC_4CN}$, $\mathrm{CH_3CHO}$.
8	$\mathrm{H_3CC_2CN}$, $\mathrm{H_2COHCHO}$, $\mathrm{CH_3OOCH}$, $\mathrm{CH_3COOH}$, $\mathrm{H_2C_6}$, $\mathrm{C_2H_6}$, $\mathrm{CH_2CHCHO}$, $\mathrm{CH_2CCHCN}$, $\mathrm{CH_3C_3N}$, $\mathit{C_7H}$, $\mathrm{H_2NCH_2CN}$.
9	$\mathrm{CH_3C_4H}$, $\mathrm{CH_3OCH_3}$, $\mathrm{CH_3CH_2CN}$, $\mathrm{CH_3CONH_2}$, $\mathit{C_8H}$ (and $\mathit{C_8H^-}$), $\mathit{HC_6CN}$, $\mathrm{CH_3CHCH_2}$, $\mathrm{CH_3CCCN}$.
10	$\mathrm{(CH_3)_2CO}$, $\mathrm{CH_3CH_2CHO}$, $\mathrm{CH_3C_5N}$, $\mathrm{HOCH_2CH_2OH}$.
11	$\mathit{HC_8CN}$, $\mathrm{CH_3C_6H}$, $\mathrm{C_2H_5OCHO}$.
12	$\mathrm{CH_3OC_2H_5}$, $\mathrm{C_6H_6}$, $\mathrm{C_3H_7CN}$.
13	$\mathit{HC_{10}CN}$.

The preparation of isotopologues of cyanoacetylene exemplifies the increasing synthetic difficulties. The synthesis of cyanoacetylene has been reported in 1910 in quite particular experimental conditions due to the high chemical reactivity of this compound: the corresponding amide **2** was mixed with sea sand and phosphorus pentaoxide (P_4O_{10}) and heated up to 200°C *in vacuo* [22]. Pure cyanoacetylene was thus evacuated as it was formed and trapped at low temperature. The pure compound is stable for years in a freezer. The deuterated derivative has been formed by addition of deuterated water and potassium carbonate as catalyst followed by the separation under nitrogen of the organic phase subsequently dried on solid P_4O_{10} in the gas phase. To synthesize the ^{15}N derivative, the labeled amide easily formed starting from the corresponding ester and ^{15}N ammonia was dehydrated [23] (Scheme 1). However, the selective synthesis of mono ^{13}C derivatives is much more challenging. $HC\equiv C^{13}CN$ has been very recently prepared in small amounts and with a small yield by the reaction of labeled p-toluenesulfonyl cyanide **3** with 1,2-bistributylstannylacetylene **4** (a reaction of exchange between a tin group and a CN group discovered in our lab for the preparation of HC_5N **5**, see below). The reaction involves the exchange around 60°C of a tin substituent with an electropositive carbonitrile group ($CN^{\delta+}$) and the homolytic breaking of the second C-Sn bond followed by the abstraction of a hydrogen radical from another molecule [24]. Here also the product is continuously extracted from the reaction mixture as it is formed to avoid its decomposition. The more evident use of a tributylstannylacetylene as precursor leads to the distillation of this latter from the reaction mixture before the reaction with the reagent. On the other hand, the synthesis of the ^{13}C labeled isotopomers on the CC triple bond ($H\text{-}^{13}C\equiv C\text{-}CN$ and $H\text{-}C\equiv {}^{13}C\text{-}CN$) has never been performed. It should be noted that no general approach in organic synthesis allows the selective labeling of a primary alkyne.



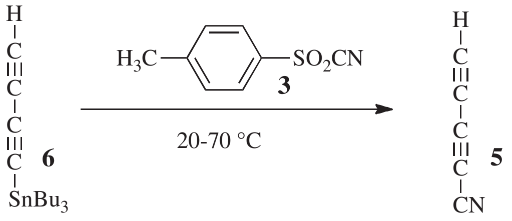
Scheme 1.

HC_5N **5**, the first cyanopolyyne, was detected for the first time in the molecular cloud Sgr B2 [25]. It has then been observed in numerous cold dark clouds [26] and in hot circumstellar environments such as CRL 618 [27, 28]. The isotopologues DC_5N [29], $HC^{13}\equiv C\text{-}C\equiv C\text{-}CN$, as well as $H\text{-}C\equiv C\text{-}C\equiv C\text{-}{}^{13}CN$ [30] have been detected in Taurus Molecular Cloud 1 (TMC-1). Attempts to detect this molecule in Titan's atmosphere were unsuccessful up to date either in the submillimeter range [31] or in the infrared and in the UV range.

Cyanobutadiyne had never been prepared in pure form up to 2005. The most important approaches were the desilylation of the corresponding trimethylsilylcyanobutadiyne [32], a discharge with a tesla coil on benzonitrile [33] and a direct-current (DC) discharge in a mixture of cyanoacetylene and acetylene [34]. In 2004, the detection of HC_5N in the thermolysis products of pyridine at 1200°C in the presence of PCl_3 [35] showed, once again, how challenging the preparation of this species was. Most of these approaches leading to mixtures of products were good enough to record the microwave spectrum of HC_5N and allowed the detection of this product and of many isotopomers in the ISM [25–30].

However, to confirm (or to disprove) models that foresee the presence of cyanobutadiyne on Titan, it was essential to have this molecule at hand. An infrared spectrum of the pure product would allow an estimation of the partial pressure of this molecule on Titan, provided it is detected there. The reaction of this compound with many reagents is of great interest in itself and by comparison with cyanoacetylene and cyanopropyne. Moreover, the synthesis of pure cyanopolyynes with the formula $H\text{-}(C\equiv C)n\text{-}C\equiv N$ is the key to a better knowledge of this family of compounds.

The reaction of tributylstannylbutadiyne **6** with excess of p-toluenesulfonyl cyanide **3** led to the cyanobutadiyne **5**, which was selectively trapped at −80°C to remove low-boiling impurities (Eq. 1). The compound was obtained in pure form but in only 15% yield. About 300 mg of cyanobutadiyne has been prepared in one experiment through this approach. Pure cyanobutadiyne can be kept indefinitely in dry ice, but decomposes slowly at −40°C in pure form or at room temperature in $CDCl_3$ [36].



(1)

Figure 1. Closed cell equipped with a Suprasil window and a stopcock.

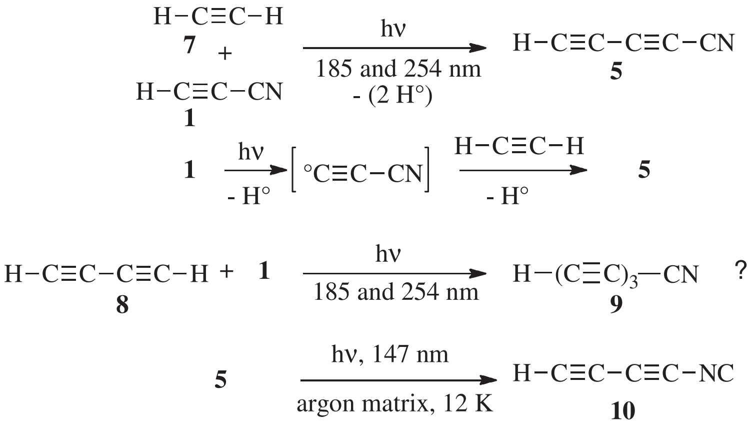
Thanks to this synthesis, the gas phase infrared and UV spectra of this compound with the intensities of the bands have been recorded [37, 38]. The deuterated derivative was prepared by an approach similar to the one reported for the deuterocyanoacetylene. H-C≡C-C≡C-^{13}CN and H-C≡C-C≡C-C^{15}N derivatives were recently synthesized by the exchange between the tin derivative and labeled p-toluenesulfonyl cyanide [39]. The synthesis of ^{13}C derivatives selectively labeled on one of the CC triple bond is still to discover. On the other hand, attempts to extend this approach to the following element HC_7N are up to now unsuccessful and this compound, potentially so useful to precise the formation of cyanopolyynes in the interstellar medium, has never been isolated up to date.

1.2 Photochemical studies concerning cyanobutadiyne

To have in hand cyanobutadiyne **5** allows to unambiguously identified it by spectroscopy (NMR, IR, HRMS, …) in various photolysis of gas mixtures and thus to propose possible precursors of this compound for the ISM or the atmosphere of Titan. However temperatures and partial pressures higher than those of these medias are necessary to be able to detect photoproducts, and the times of photolysis are far from the billions of years of irradiations already performed in these medias. Consequently, and even using a flow system, the lab experiments can only propose some reaction pathways to explain the nature of the photoproducts, but the extrapolation to the ISM or planetary atmospheres has to be performed carefully.

As an example, the photolysis at 185 and 254 nm of cyanoacetylene **1** and acetylene **7** mixtures at room temperature in a closed cell (Fig. 1) leads to cyanobutadiyne. The compound was identified by ^{1}H NMR spectroscopy by its chemical shift and then the addition of an authentic sample to support its presence by the observation of only one signal. In the photolysis of mixtures of cyanoacetylene and butadiyne **8**, the NMR signal was observed a few more at down-field and was tentatively attributed to the following cyanopolyyne: HC_7N **9**. However, only the synthesis of an authentic sample could confirm its presence. Such products being formed using a 185 and 254 nm lamp and not with a 254 nm lamp only, a reaction pathway involving the breaking of the C-H bond of cyanoacetylene [40], followed by an addition-elimination was proposed (Scheme 2). On the contrary of cyanoacetylene [41], the photolysis of cyanobutadiyne by itself at 185 and 254 nm did not give well-identified products and only dusts were observed [42] (probably oligomeric compounds like those observed in the photolysis of cyanoacetylene

[41b]), Using a 147 nm lamp, the photolysis of a co-deposited sample of Argon and HC_5N cooled at 10 K led to the observation of several isotopomers and, in particular, of the corresponding isonitrile **10** [38, 43].

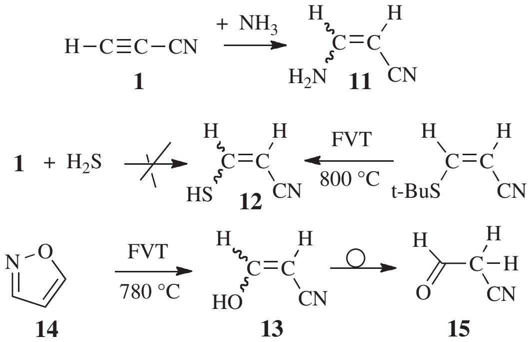


Scheme 2.

1.3 Adducts of cyanoacetylene

Cyanoacetylene is supposed to be a good starting material for the formation of new, more complex, astrochemical species [44], or amino acids on primitive Earth [14] but which products are formed in the first step? Even if it is difficult to predict the nature of these compounds, a general study on addition of various simple components (ammonia, water, hydrogen sulfide, for example) can be performed and is useful for identifying the compounds which are formed or not in such reactions. Such adducts could be present in the ISM, in comets or could have played a role in prebiotic chemistry. At room temperature, the addition of ammonia on HC_3N gives the 3-amino-2-propenenitrile (aminoacrylonitrile) **11** in some hours [41, 45]. However this reaction probably cannot be performed at low temperature without irradiation. Addition of H_2S on cyanoacetylene only occurs in the presence of a base or under irradiation but only a diadduct, the sulfide, was obtained in our lab conditions even when using a huge excess of hydrogen sulfide. The 3-mercapto-2-propenenitrile **12** was prepared by flash vacuum thermolysis (FVT) of the t-butyl derivative [46]. The FVT is based on the vaporization *in vacuo* of a precursor in a short oven heated at a temperature ranging between 400 and 1200°C (Fig. 2). On the other hand, in possible prebiotic conditions, water adds on cyanoacetylene in the presence of a base like sodium hydroxide to form the 3-hydroxy-2-propenenitrile (cyanovinylalcohol) **13** [47]; cytosine and uracil were subsequently formed by addition of urea or cyanate respectively. To isolate this cyanovinylalcohol on a preparative scale, an original approach had to be found: the FVT of a cyclic isomer, the isoxazole **14**. However, the formed cyanovinylalcohol quickly rearranges to form the cyanoacetaldehyde **15** [48]. The stability of these three adducts of cyanoacetylene was good enough to keep them in a freezer (−30°C) under nitrogen.

Very little is known about the chemistry of these and other similar cyanovinyl derivatives. Indeed, there is a complete lack of information regarding their intrinsic reactivity. The introduction of a cyano group in a conjugative position in vinylamine ($H_2C{=}CH\text{-}NH_2$) dramatically modifies the properties of the unsaturated amine. Thus, although vinylamine is unstable at −80°C in the condensed phase and decomposes in the presence of several reactants, aminoacrylonitrile is a kinetically quite stable compound. The approaches reported above allowed recording the gas phase infrared spectra of these three compounds and their microwave spectra at room temperature [45, 46, 49, 50]. The spectra have been given to observatories to help to their detection in the ISM, provided they are present. By FT-ICR, the acidity and basicity of these compounds were measured and compared with those



Scheme 3.

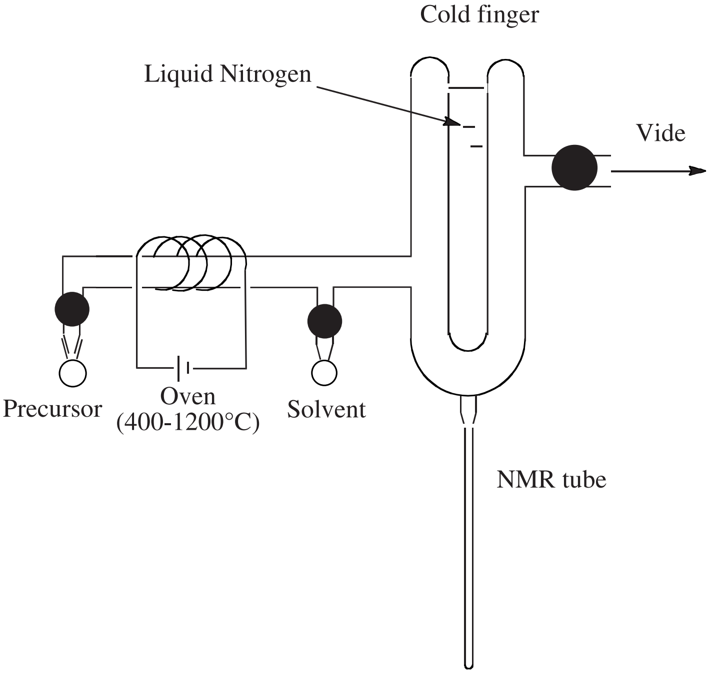
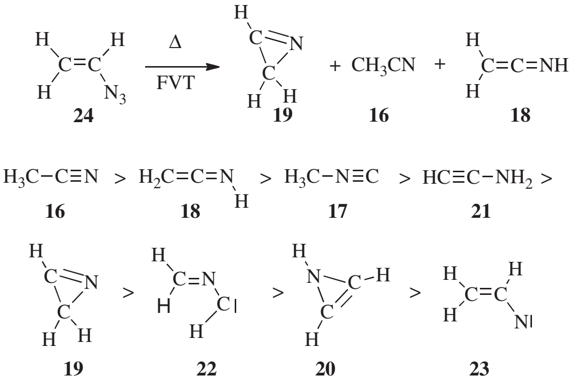


Figure 2. Schematic representation of a FVT apparatus.

of propenenitrile and other heterosubstituted heteroacrylonitriles (X = PH_2, SiH_3). For the neutral molecules, under standard gas-phase conditions at 298 K, the Z-isomer is always the dominant species. The cyanovinyl derivatives have a significantly stronger gas-phase acidity than that of the corresponding vinyl compounds $CH_2{=}CH\text{-}X$. This acidity-strengthening effect of the cyano group is attributed to the larger stabilization of the anion with respect to the corresponding neutral compound. The loss of the proton from the substituent X was found to be systematically much more favorable than the deprotonation of the HC=CH linking group. The corresponding E isomeric ion is much more stable than the Z-one, so that only the former should be found in the gas-phase. For the basicity, push-pull effects explain the preference of aminoacrylonitrile to protonate at the cyano group, which also explain the relatively high basicity of this derivative as compared to the other members of the set analyzed, which present rather similar gas-phase basicities: GB $\approx 780\,\text{kJ mol}^{-1}$, indicating that the different nature of the substituents has a weak effect on the intrinsic basicity of the cyano group [51]. This push-pull effect was also observed by photoelectron spectroscopy [52].

2. ISOMERS OF ACETONITRILE

Several isomers with a C_2H_3N formula can be drawn like acetonitrile **16** (CH_3CN), methyl isonitrile **17** (CH_3NC), ketenimine **18**, 2H-azirine **19**, 1H-azirine **20** and ethynamine **21**. Acetonitrile **16**, methyl isonitrile **17** and, more recently, ketenimine **18** have been detected in the ISM [53, 54]. The relative thermodynamic stability of these compounds, determined in 1983 by MNDO calculations and using the GAUSSIAN03 package in 2009, gives the acetonitrile **16** unambiguously as the most stable isomer followed by ketenimine **18** and then methyl isonitrile **17** [55]. The ethynamine **21** seems to be thermodynamically more stable than the 1H-azirine **19**, followed by a carbene **22** ($CH_2{=}N\text{-}CH$), the 1H-aziridine **19** and the methyl nitrene **23** (Scheme 4). Confrontation between calculations and observations shows that when several isomers of the same generic formula are identified, it is always the most stable one that is the most abundant in the ISM [56]. Moreover, the abundance ratio of the most stable isomer to the other isomers is directly related to their energy difference. In the case of the isomers of C_2H_3N, the detection of each one is correlated to our ability to prepare them and to record their spectra. Acetonitrile is commercially available and is used at an industrial level. Methyl isocyanide is easily synthesized by dehydratation of the corresponding formamide [57]. Ketenimine has been detected in the flash vacuum thermolysis products of vinylazide **24**, an explosive compound, and its microwave spectrum has been recorded [58] but 2H-azirine is the main product of this reaction with acetonitrile as by-product [59]. 1H-azirine and ethynamine have never been isolated but the latter has been detected by photoelectron spectroscopy [60]. So the IR and MW spectra of both compounds, so helpful to allow their detection if they are present in the ISM, have never been recorded. For nitrenes or carbenes, only the generation and analysis in the gas phase can be envisaged.



Scheme 4.

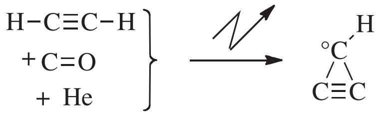
3. STUDIES ON ANIONS, CATIONS AND RADICALS

Many studies can be performed at very low temperature in the solid phase on ions or radicals. However the characte-rization of gases in the clouds of the ISM can be only confirmed by a comparison with the MW or IR spectra recorded in labs and performed with samples in the gas phase. Many components of the ISM are radicals, anions or cations (see Table 1) and it is not possible to synthesize, condense and then vaporize them in the cell of the spectro-meter. So it is necessary to generate such compounds in the gaseous phase and to analyze directly the gaseous flow of the pure product or often of a mixture of compounds. Some examples are reported below. A high voltage pulsed discharge can produce just about any unstable molecule as long as the required elements are present in the gas mixture or in the single precursor.

The carbon chain radicals CCCCH (butadiynyl) and CCCN (cyanoethynyl) were first detected in the gas phase with a radiotelescope [61, 62] in the molecular envelope of the carbon-rich star IRC110216, and these isoelectronic radicals were subsequently observed in low pressure laboratory gas discharges

[63]. The millimeter-wave rotational spectra of the CCCCH and CCCN radicals and their isotopic species were measured and the rotational, centrifugal distortion, and spin-rotation constants determined [64]. Free CCCCH was produced in a DC glow discharge (~0.6 A) through helium and acetylene at a temperature of 120 K and pressure of 30-40 mTorr. The ^{13}C species of CCCCH were observed when ^{13}C-enriched carbon monoxide was added to the discharge in the molar ratio helium: acetylene: carbon monoxide of 7:14:4. Free CCCN was produced in a DC discharge (~0.4 A) through nitrogen and acetylene in molar ratios of 10:7 at a temperature of 120 K and pressure of 40 mTorr.

On the other hand, the rotational spectral lines of the cyclic C_3H radical in the $^2B_2$ ground electronic state were observed by MW spectroscopy [65]. The radical is produced in an absorption cell by discharging a mixture of C_2H_2, CO, and He (Eq. 2). The spectral lines of two ^{13}C isotopic species are also observed. The radical is a planar molecule with C_{2v} symmetry.



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Anions and cations can also be generated by similar approaches. Degenerate four-wave mixing (DFWM) has been used to record the spectra of charged and neutral carbon-containing radicals generated in a pulsed discharge source within a supersonic slit-jet expansion. The DFWM method allows a selective molecular detection by varying the discharge timings. Gas mixtures used for the production of the HC_2S and C_4H radicals were $CS_2/C_2H_2/Ar$ (0.5/1/98.5%) and C_2H_2/Ar (1/99%), respectively. For the production of the diacetylene cation, the precursor was C_2H_2 (or C_4H_2) diluted in argon. The methods were successfully used for the detection of C_4H, HC_2S, and HC_4H^+ with signal-to-noise in the range of 10^2–10^4 [66].

As another example, samples of OD^- have been produced by a positive as well as a negative glow discharge (≈1500 V and a few mA) inside the absorption cell starting from D_2 and O_2, in the ratio of 1:3. The rotational spectrum of the molecular anion OD^- has been observed by microwave spectroscopy and identified by the Doppler-shift effect. Analogously, samples of N_2H^+ have been produced starting from H_2 and N_2, in the ratio of 1:3, by applying the same DC discharge [67].

The recent discovery of cyanoacetylide $CCCN^-$ [68] in an expanding envelope around the carbon star IRC+10216, which is added to previous circumstellar/interstellar detections] of $(CC)_nC_2H^-$ species ($n = 1 - 3$) [69–71], isoelectronic with $(CC)_nCN^-$, makes all such species important astrochemical objects. Anions of these families are also potentially important constituents of Titan's ionosphere [72].

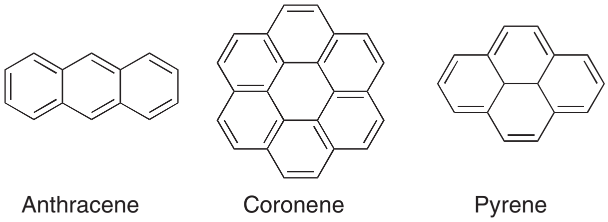
The C_6H^- anion was produced by a 600 V low-current (~20 mA) gas discharge synchronized with a gas pulse 330 ms long (yielding a flow of 25 cm^3 $minute^{-1}$ at standard temperature and pressure), the gas sample consisting of either acetylene or butadiyne (0.10%) heavily diluted with Ne at a stagnation pressure of 2.5 ktorr behind the pulsed valve of the nozzle. Butadiyne produced the stronger lines [73]. In similar experiments, the rotational spectra of C_3N^-, C_4H^-, and C_4D^- have also been measured at high-spectral resolution by Fourier transform microwave spectroscopy [74]. C_3N^- was generated starting from butadiyne and cyanoacetylene.

In all these experiments involving gas discharge, only tenths of % of the expected product are produced and the gaseous flow contains this compound in concentrations of tenths to hundredths of %. However with the help of the theoretical calculations, many lines of the MW spectra can be attributed and used for the detection in the ISM of these species, never isolated and never condensed in the labs.

4. LARGE MOLECULES, OLIGOMERS AND POLYMERS

Between the small molecules and the grains or dusts, many large molecules, oligomers and polymers are present in the ISM, in comets or planetary atmospheres. With a low vapor pressure at low temperature, the gaseous part of these compounds can only be very small. Even if such compounds are not the topic of this article, we have to recall the presence of components which lie between the molecules with a small number of atoms and the grains or dusts.

Polycyclic Aromatic Hydrocarbons (PAHs) are a class of compounds with only C and H atoms and several benzene rings. As examples can be cited anthracene, coronene or pyrene (Scheme 5).



Scheme 5.

PAHs were proposed to account for the well-known IR Bands between 3.3 and 12.7 microns observed in the ISM [75]. Although no specific PAH molecule has been identified up to date, the astrophysics community largely accepts the hypothesis that PAHs are a part of the interstellar dust grains and that they play a major role in the ISM. Probably the ISM contains thousands of different PAHs in various abundances. Many infrared spectra of mixtures of these compounds fit well with the spectra of the ISM [76, 77]. Due to the high similarities of all these compounds between them, it has not been possible up to now to differentiate unambiguously between the systems. On the other hand, the permanent dipolar moment of such compounds is too weak to envisage their detection by microwave spectroscopy.

The case of tholins is quite different. For example, tholins are formed in the upper atmosphere of Titan by the photolysis at low wavelength of CH_4-N_2 mixture maybe in the presence of other minor compounds. Monomeric, oligomeric and polymeric products are formed and probably tholins contain impressive amounts of compounds differing in molecular weight, the nature of atoms and functions. Attempts to prepare tholins in the lab led to complex mixtures of products, never totally identical to those of the previous preparations, and which cannot easily be analyzed. Thus, a laboratory analogue of Titan's haze was formed in an inductively coupled plasma from nitrogen/methane = 90/10 gas mixture at various pressures ranging from 13 to 2300 Pa [78]. Powdered samples of carbon–nitrogen-hydrogen "tholins" that mimic Titan's atmosphere aerosols were also produced under levitation conditions in the laboratory with a dusty plasma (PAMPRE experiment) using different initial N_2:CH_4 gas mixtures [79]. Chemical and optical properties of the resulting tholins depend on the parameters of the experiments. The partial reproducibility of such preparations has dramatically limited our understanding of the composition of tholins since several decades. Even if functional groups can be identified, only a macroscopic definition of these mixtures of compounds can be envisaged.

PAH and tholins have generated many studies to attempt to understand the composition of such complex mixtures of products. Independently of our inability to dispose of dusts from Titan or the ISM, the understanding of these mixtures of compounds will necessitate to characterize them by data between those of the analysis of monomeric compounds and those of polymers and this in function of our partial knowledge of the physicochemical parameters of their formation in these media.

5. CONCLUSION

With the future space missions, we will have a better knowledge of the composition of the atmospheres of Planets or of the molecules in the ices of comets, and new interstellar molecules will be discovered. Many simple compounds, potential candidates of these medias have never been isolated like aminol (H_2NCH_2OH), aminal ($H_2NCH_2NH_2$), carbamic acid (CH_3NHCO_2H), many isomers or higher homologues of observed molecules. The synthesis of new compounds, the recording of their spectra, their unambiguous identification in photoproducts are some of the numerous studies we have to perform. The chemistry of the ISM, the comae, the planetary atmospheres will give new and exciting problems in synthetic chemistry for many decades. We will have again and again to reconsider our scientific convictions on the basis of the new discoveries to understand the fascinating chemical evolution of these media.

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